PATENT SPECIFICATION

COMPLETE SPECIFICATION

Ethylene Interpolymer Latex

We, UNION CARBIDE CORPORATION, of 270, Park Avenue, New York, State of New York, United States of America, a Corporation organised under the laws of the State of New York, United States of America, (Assignee of DONALD WAYNE SIMROTH), do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates in general to latices of ethylene interpolymers. More particularly, this invention relates to a novel continuous emulsion polymerization process for producing ethylene interpolymers in latex form and to the novel latex products produced thereby. In a particular aspect, the invention also relates to utilization of the novel latex products in coating of paper and paper products to impart desirable properties thereto.

For many years research efforts have been directed toward production by emulsion polymerization techniques of ethylene polymer latices exhibiting a combination of both good latex properties and good polymer properties and thereby meeting the stringent requirements imposed by commercial utilization in, for example, coating applications such as paper coating. The attributes of a high quality latex suitable for use in coating applications are well known. Thus, for example, the polymer particles must be sufficiently small, e.g. below about one micron, to permit the formation of a coherent coating on drying; the total solids content must be high, e.g. at least 40 per cent solids, so that the amount of water which must be evaporated will not be excessive; the latex viscosity must be low, e.g. below 300 centipoises, and the flow properties those of a non-dilatant fluid so that the latex can be easily pumped and handled; the amount of scrap or seeds, i.e. particles larger in size than the maximum within the permissible range for a latex, must be low, e.g. below 200 parts per million on 100 mesh screen, based on the total weight of the latex; and, finally, the latex must be stable on standing for long periods of time, e.g. a year or more, and stable to freeze-thaw, mechanical, and chemical stress. Of equal importance to the properties of the latex are the properties of the polymer itself. Thus, for example, in coating applications it is often necessary that the coating possess strength and toughness and be impervious to moisture and unless the polymer possesses these characteristics in sufficient degree the latex will be of little value even though it exhibits excellent latex properties such as fluidity and stability. Moreover, since it is not ordinarily feasible with a latex produced directly by emulsion polymerization to free the latex from contaminants introduced in the polymerization, such as the surfactants which are needed to promote the initiation of new polymer particles and to aid in stabilizing the latex, these will become an integral part of the coating which is formed upon evaporation of the water from the latex. Accordingly, the coating must possess the required strength, toughness and impermeability in spite of the presence of contaminants introduced in the polymerization process which will inevitably detract from such properties.

Heretofore, efforts to produce an ethylene polymer latex having the desired combination

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of properties have been unsuccessful, the product either being deficient in the qualities that characterize a good latex or deficient in essential polymer properties.

It has long been known that persulfate compounds are effective catalysts for the emulsion polymerization of ethylene to form solid homopolymers, copolymers, or terpolymers, and that the resulting emulsions ordinarily exhibit good latex qualities, e.g. stability. However, it is also well known to the art that the use of these catalysts under conventional emulsion polymerization techniques results in the formation of a polymer with poor physical characteristics, e.g. low strength and a lack of flexibility, so that the latex is unsuited for use in coating applications.

It has now been discovered that emulsion polymerization can be effected, in accordance with the teachings herein, utilizing a persulfate compound as catalyst to produce an ethylene interpolymer latex exhibiting the long sought combination of good latex properties and good polymer properties.

In accordance with this invention, a minor proportion of a carboxylic acid is copolymerized with ethylene to promote latex stability, and thereby permit the amount of surfactant utilized in the emulsion polymerization to be held to a minimum. This materially aids the achievement of desirable polymer properties such as strength and toughness, since a lesser amount of surfactant will be present as a contaminant of the coating and the detrimental effect on polymer properties will thereby be reduced. The exact mechanism whereby the presence of a minor amount of carboxylic acid as a component of the ethylene interpolymer promotes latex stability is not known, but it is believed that the acid groups at the surface of the polymer particle will be surrounded by water molecules bound thereto by hydrogen bonding and that this "shell" of water makes it more difficult for two polymer particles to coalesce with a resulting increase in latex stability. The presence of a carboxylic acid component also provides an added advantage in that the adhesion of the latex to various substrates is markedly enhanced. As well as ethylene and one or more carboxylic acids, the interpolymers of this invention may also contain, if desired, one or more additional copolymerizable monoethylenically unsaturated monomers, as hereinafter described in greater detail.

A further important characteristic of the novel emulsion polymerization process of this invention is the use of high temperatures and high pressures, as hereinafter described in detail, whereby high reaction rates and, consequently, high space productivity are achieved. Under the conditions of pressure and temperature utilized, the polymerization reaction proceeds extremely fast. Since the polymerization reaction is highly exothermic, the result is the rapid generation of large quantities of heat; however, since the reaction temperature is high, a large temperature differential exists across the cooling surface of the reactor wall and the heat generated can be effectively removed to thereby permit close control of the reaction.

A further important characteristic of the novel emulsion polymerization process of this invention is the utilization of an exceptionally high rate of throughput. At the high temperatures necessarily employed in the process to achieve the desired high production rate and promote heat removal, the persulfate catalyst, necessarily employed to achieve the desired latex stability, decomposes at an extremely fast rate. Accordingly, the polymerization must be accomplished rapidly so that the persulfate catalyst will not be consumed prematurely with the result that no appreciable degree of polymerization will take place. This is successfully achieved by the use of high temperatures and pressures, which accelerate the reaction, and by high feed rates per unit of reactor volume combined with the use of a reactor adapted to permit thorough mixing to give substantially uniform reaction conditions.

In brief, the process of this invention provides for the first time a method of producing an ethylene interpolymer latex possessing a combination of good latex properties and good polymer properties and being eminently suited for use in coating applications. Furthermore, the method herein described achieves this result in a continuous process with high productivity and high conversion per pass which render it economically feasible for use in large scale commercial operations. Such a result is achieved through the utilization of a unique combination of operating conditions providing an emulsion polymerization process radically different from any known heretofore.

The ethylene interpolymers within the scope of this invention are (1) copolymers or higher interpolymers of ethylene with at least one α,β-ethylenically unsaturated carboxylic acid of 3 to 8 carbon atoms and (2) terpolymers or higher interpolymers of ethylene, the aforesaid carboxylic acid, and at least one copolymerizable monoethylenically unsaturated monomer of 2 to 12 carbon atoms, other than an α,β-ethylenically unsaturated carboxylic acid. Illustrative of the carboxylic acids contemplated are acrylic acid, methacrylic acid, ethacrylic acid, itaconic acid, crotonic acid, isocrotonic acid, maleic acid, fumaric acid, and the like. Illustrative of the copolymerizable monomers contemplated are vinyl esters of alkanoic monobasic acids having up to 4 carbon atoms such as vinyl formate, vinyl acetate, vinyl propionate, vinyl n-butyrate, vinyl isobutyrate, and the like; vinyl and vinylidene halides such as vinyl chloride, vinyl fluoride, vinylidene chloride, and the like; acrylates and methacrylates such as methyl acrylate, methyl metha-

crylate, ethyl acrylate, ethyl methacrylate, n-propyl acrylate, n-butyl acrylate, isobutyl acrylate, n-hexyl acrylate, 2-ethylhexyl acrylate, glycidyl acrylate, bicyclo[2.2.1]hept-2-yl acrylate, and the like; dialkyl maleates and fumarates such as dimethyl maleate, diethyl maleate, dibutyl maleate, dibutyl fumarate, and the like; acrylonitrile; N-vinyl pyrrolidone; bicyclo[2.2.1]hept-2-ene; and the like.

The continuous emulsion polymerization process of this invention involves continuously charging to a reactor, operated at high temperature and pressure and with thorough mixing to maintain substantially uniform conditions of temperature, pressure and concentration throughout, the polymerizable monomers, water, a persulfate catalyst, and one or more surfactants, and continuously recovering the latex produced. The exact manner in which the several components are charged to the reactor, or the particular type of reactor utilized, are not critical features of this invention. Thus, for example, the several components can be charged separately or in various combinations and the process can be conducted using a single stirred reactor, two or more stirred reactors in series, a loop reactor, or a tubular reactor with a plurality of injection points along its length to compensate for differences in rate of polymerization of the various monomers, as would be understood by one skilled in the art of polymerization. A convenient procedure is to charge the water, surfactant and catalyst in one stream, the ethylene as a second stream, and the carboxylic acid and, if desired, additional polymerizable comonomer, as a third stream. If desired, the carboxylic acid may be added as a solution in water or in an organic diluent and various modifiers or additives, such as, for example, molecular weight regulators, may also be charged to the reactor.

Operating temperatures within the scope of this invention are in the range of from 100° C. to 160° C., and more preferably in the range of 110° C. to about 150° C. Temperatures of significantly below 100° C. do not provide sufficiently high reaction rates, or a sufficient temperature differential for heat transfer, to be utilized in a commercially feasible process, while temperatures significantly above 160° C. cause excessively fast decomposition of the persulfate catalyst, so that it may be decomposed before it reaches the locus of polymerization. While it is ordinarily desirable to utilize the highest temperature possible, within the above range, so as to maximize heat transfer and optimize the physical properties of the polymer, the optimum temperature for the process is dependent upon the particular catalyst and surfactant employed and upon the composition of the particular interpolymer being produced. Thus, for example, with an ethylene/vinyl acetate/acrylic acid terpolymer, it is usually desirable to keep the temperature in the range of 110°

C. to 120° C. to avoid excessive crosslinking or branching which results in the formation of a polymer which is lacking in strength.

The process of this invention is conducted at a pressure of at least 5,000 psig. and preferably at least 10,000 psig. The main effect of an increase in pressure is to increase the reaction rate and since there are no significant detrimental effects accruing to the use of high pressures the process is ordinarily operated at the highest pressure which is practical as dictated by the requirements of safety and economics. Thus, pressure in the range of 5,000 psig. to 50,000 psig., or more, may be used, but striking a balance between the competing considerations will ordinarily indicate the use of a pressure in the range of 10,000 to 30,000 psig.

The ethylene, the carboxylic acid, and, optionally, the copolymerizable monoethylenically unsaturated monomer are charged to the reactor in proportions depending upon the desired composition of the ethylene interpolymer. As employed herein and in the appended claims, the term "polymerizable monomer" is used to refer to the total charge to the reactor of ethylene, carboxylic acid, and copolymerizable monoethylenically unsaturated monomer. Thus, the polymerizable monomer may consist of, for example, ethylene and acrylic acid; or ethylene and methacrylic acid; or ethylene, ethyl acrylate and acrylic acid; or ethylene, vinyl acetate, and acrylic acid; or ethylene, methyl methacrylate and methacrylic acid; or ethylene, acrylic acid, ethyl acrylate and glycidyl acrylate; and so forth. To produce the ethylene interpolymers contemplated herein, the polymerizable monomer charge to the reactor will consist of at least 50 mole per cent ethylene and from 0.2 to 15 mole per cent of a carboxylic acid, as hereinbefore defined, with any remaining balance being a copolymerizable monoethylenically unsaturated monomer, as hereinbefore defined. Thus, the polymerizable monomer might, for example, consist of 99 per cent ethylene and 1 per cent acrylic acid; or 90 per cent ethylene and 10 per cent methacrylic acid; or 85 per cent ethylene and 15 per cent acrylic acid; or 70 per cent ethylene, 15 per cent acrylic acid and 15 per cent ethyl acrylate; or 50 per cent ethylene, 10 per cent acrylic acid and 40 per cent vinyl acetate; or 60 per cent ethylene, 5 per cent acrylic acid, 20 per cent ethyl acrylate, and 15 per cent glycidyl acrylate; and so forth (all illustrative compositions given being in mole per cent). Preferably the copolymer consists of at least 90 per cent by weight ethylene and the balance acrylic acid.

The rate at which polymerizable monomer is charged to the reactor in accordance with this invention is a rate of at least 50 lbs. per hour per cubic foot of reactor volume, and preferably a rate in the range of 100 to 300 lbs. per hour per cubic foot of reactor volume.

This is the total rate of the combined charge of all of the monomers, i.e. ethylene plus carboxylic acid plus any other copolymerizable monomer optionally included. The maximum rate at which polymerizable monomer can be fed is limited primarily by the necessity of dissipating the large amount of heat generated by the polymerization reaction and is thus, in part, determined by reactor design. Operation at a rate below the minimum specified is uneconomical and frequently also undesirable from the viewpoint of the physical properties of the resulting latex.

Water is charged to the reactor in an amount dependent upon the rate of charge of polymerizable monomer and upon the desired solids content of the ethylene interpolymer latex. Latices having the desired combination of properties described herein can be produced by charging the reactor with water at a rate of 0.3 to 3 lbs. per lb. of polymerizable monomer undergoing conversion to polymer, and more preferably 0.8 to 1.5 lbs. per lb. of polymerizable monomer undergoing conversion to polymer.

As indicated hereinbefore, the novel emulsion polymerization process of this invention utilizes a persulfate compound as catalyst. More specifically, the catalyst employed is selected from the group consisting of ammonium persulfate ($(NH_4)_2S_2O_8$) and alkali metal persulfates, e.g. sodium persulfate ($Na_2S_2O_8$) or potassium persulfate ($K_2S_2O_8$). The preferred catalyst is potassium persulfate. These compounds are well known emulsion polymerization catalysts and function as water-soluble, oil-insoluble, free radical initiators. Oil-soluble, water-insoluble, free radical initiators such as organic peroxides, which are also well known and widely used catalysts in emulsion polymerization, are not suitable for use in the process of this invention as they will not yield a stable latex.

The persulfate compounds utilized as catalysts decompose rapidly under the reaction conditions of the process. The half-life, i.e. the time required for one half of the catalyst to decompose, for potassium persulfate at various temperatures is approximately as follows:

Temperature (°C.)	Half-Life (seconds)
100	700
125	40
150	3
160	1

It is accordingly apparent that to successfully utilize these catalysts at the process temperatures hereinbefore disclosed conditions must be maintained which permit the polymerization reaction to be carried out extremely fast, i.e. high pressures, thorough mixing, effective heat removal, and high throughput.

The amount of catalyst employed is not critical as long as it is present in sufficient concentration to promote the polymerization, i.e. a catalytically effective amount. An amount of at least 0.001 lbs. per lb. of polymerizable monomer undergoing conversion to polymer is ordinarily required. Generally speaking, amounts of from 0.001 to 0.02 lbs. per lb. of polymerizable monomer undergoing conversion to polymer are employed, with preferred amounts being in the range of 0.002 to 0.007 lbs. per lb.

The use of a surfactant is an essential feature of the polymerization process described herein. The surfactant serves a dual function in that it assists in the initiation of new polymer particles and also helps to stabilize the latex. However, from the standpoint of the end use of the latex, e.g., in paper coating, the use of a surfactant in the process is usually highly detrimental since it will end up as a contaminant of the coating and will adversely affect the properties of the polymer. Accordingly, it is desirable that the concentration of surfactant be held to a minimum and it is one of the unique features of this invention that a stable, high quality latex can be produced with a far lower total content of surfactant than has been necessary in processes for production of ethylene polymer latices known heretofore.

The use of particular surfactants is not critical to successful operation of the process of this invention. The sole essential requirement is that the surfactant be chemically stable and capable of forming abundant micelles under the operative conditions of the process. As is well known in the polymer art, the formation of micelles, i.e. small clusters of surfactant molecules, is necessary to the formation and growth of the polymer particles composing a latex. The usual theory is that the micelle has the hydrocarbon portion of all the molecules of surfactant in a central organic phase and the ionic or salt portion in a surrounding water phase. Polymer is then formed from monomer which is absorbed in the central organic portion and the micelle is enlarged by the polymer formation until the final particle size is reached. The concentration of surfactant at which micelles begin to form in detectable quantities is called the critical micelle concentration and is dependent upon the structure of the surfactant and upon the temperature.

A single surfactant or a mixture of two or more surfactants may be employed in the process of this invention. The particular compounds to be used will be dictated primarily by the subsequent application for which the latex is intended, for example, if the latex is to be used to form a coating which would come in contact with foodstuffs then toxicological properties of the surfactant would be a prime consideration. Anionic surfactants

are particularly effective, especially those that have a low critical micelle concentration at room temperature, e.g. 0.1 weight per cent or less. A combination of an anionic surfactant and a non-ionic surfactant may be employed, and such combination has been found to be particularly effective in promoting latex stability in the presence of multivalent metal ions such as calcium, magnesium or aluminum.

Particular classes of anionic surfactants that may be advantageously employed in the process of this invention are the amine or alkali metal salts of alkylaryl sulfonates, such as sodium dodecylbenzenesulfonate, the isopropylamine salt of dodecylbenzenesulfonic acid and the like; and the bis(alkyl)sulfosuccinates such as sodium bis(octyl)sulfosuccinate, sodium bis(tridecyl)-sulfosuccinate, and the like.

The amount of surfactant employed must be sufficient to effect the dual functions of assisting in the initiation of new polymer particles and aiding in stabilizing the latex which is formed. However, consistent with these requirements, it is ordinarily desirable to employ the smallest amount of surfactant possible and thereby minimize the detrimental effects of the surfactant on polymer properties. Amounts of surfactant in the range of 0.005 to 0.05 lbs. per lb. of polymerizable monomer undergoing conversion to polymer are operable, while preferred amounts are in the range of 0.01 to 0.03 lbs. per lb. of polymerizable monomer undergoing conversion to polymer.

Since the ethylene interpolymer latices within the scope of this invention always contain some carboxylic acid the pH in the reactor must be maintained at a low level to avoid inhibition of the polymerization reaction. Ordinarily the pH will be maintained at a level of below 4 and preferably below 3. After the latex leaves the reactor, it is generally desirable to increase the pH to 7 or higher, by, for example, addition of ammonium hydroxide, potassium hydroxide or sodium hydroxide, in order to minimize corrosion problems and to help stabilize the latex in storage.

As indicated hereinbefore, thorough mixing is an important feature of the novel process described herein. Under optimum conditions the reactor charge should be completely mixed within the half-life of the catalyst. Since the process is operated under conditions providing very high space productivities, it is feasible to use a small reactor wherein high agitation and rapid mixing providing substantially uniform conditions throughout the reactor can be readily achieved.

Generally speaking, the process of this invention is operated so as to provide relatively high conversion of monomers to polymer since the higher the conversion the better the economics of the process will be. If conversion is too low, the large amount of unreacted monomer causes the formation of appreciable scrap in the latex, whereas if the conversion is too high the strength of the polymer is adversely affected. The process is, accordingly, operated at the highest conversion compatible with production of a high quality product. In terms of ethylene, the conversion is typically in the range of 40 to 90 per cent, i.e. 40 to 90 per cent of the ethylene charged to the reactor is converted to polymer. More frequently, the conversion of ethylene will be in the range of 60 to 80 per cent. Since the carboxylic acid component generally polymerizes much more rapidly than ethylene under the same conditions, the conversion of the acid will ordinarily be substantially complete, e.g. 98 per cent or more. The optional copolymerizable monomer will generally also polymerize more rapidly than ethylene so the degree of conversion of such monomer will usually exceed that of the ethylene.

The flow rates of the several components charged to the reactor, as set forth hereinabove, are such that the residence time in the reactor is relatively brief. Actual residence time, is, of course, not a single value but rather there is a wide distribution of actual residence times; however, the nominal residence time may be calculated from the feed rates and the reactor volume. Under the operating conditions described herein, the nominal residence time, i.e. the value obtained by dividing the reactor volume in ft.^{3} by the total volumetric feed rate in ft.^{3}/hr., is ordinarily below 0.5 hours and ranges down to as low as 0.1 hours, or less.

The process of this invention is characterized by selection of process conditions, within the limits specified hereinabove, to provide a space productivity of at least 25 lbs. of polymer per hour per cubic foot of reactor volume. Typically, a space productivity in excess of 50 and up to as high as 200 lbs. of polymer per hour per cubic foot of reactor volume, or even higher, can be achieved by optimization of process conditions.

Ethylene interpolymer latices produced by the process of this invention meet or exceed all minimum standards of a high quality latex and are well suited to use in coating applications.

The size of the polymer particles in the ethylene interpolymer latices of this invention is in the range recognized by the art as characterizing a latex, i.e. below one micron, and ordinarily there is a broad particle size distribution. This latter feature is particularly advantageous where the latex is to be used to form a barrier coating on paper since it promotes denser packing of the particles and thereby facilitates fusion to a coherent impermeable film which effectively resists water vapor penetration. In ethylene interpolymer latices produced in accordance with the teachings herein, substantially all of the polymer

particles are in the size range of from 0.01 to 1 micron, with the average particle size being in the range of 0.15 to 0.7 microns.

The total solids content of the latices described herein will usually exceed 40 per cent and solids content of well above this value, e.g., in the range of 50 to 60 per cent and, in some instances, even higher can be achieved by control of the process variables. Accordingly, the novel latices are well suited to coating applications where a high solids content is essential to minimize the amount of water which must be evaporated.

To be useful in coating applications, latices must be amenable to being pumped and must be readily handled with conventional coating equipment. This requires that the latex have a low viscosity and that it be non-dilatant, i.e. the viscosity should not increase with increasing rate of shear. The novel ethylene interpolymer latices of this invention meet these criteria since they have low viscosities, generally below 300 centipoises, and exhibit Newtonian or pseudoplastic flow properties.

While all latices contain a certain amount of scrap or seeds, i.e. particles that are appreciably above the siz range permissible for latex particles, the amount which can be tolerated in a commercial product is usually not in excess of 200 parts per million on 100 mesh screen, based on the total weight of the latex, or up to several hundred parts per million on 250 mesh screen. The latices of this invention usually have seed contents meeting these limits and in many instances well below the maximums specified.

An important feature of the novel ethylene interpolymer latices of this invention is their unusually good stability. Thus, the latices possess excellent shelf stability, i.e. they do not undergo creaming, gelling, or thickening even after very long periods of storage such as a year or longer; which property greatly facilitates their transportation, storage and use. The latices also exhibit excellent mechanical stability, i.e. the particles do not coalesce or agglomerate when subjected to mechanical stress such as that imposed by agitation or shearing forces encountered in coating operations. The freeze-thaw stability of the latices is also good, i.e., the latex may be frozen and thawed several times without any significant change in properties resulting and thus need not be handled in any special manner merely because it will encounter extremes of temperature. Finally, the latices exhibit good chemical stability, i.e. they have good salt and solvent tolerance and are thus not easily harmed by the incorporation of additives, although they can be coagulated under severe conditions by addition of certain salts, e.g. salts of multivalent metal ions such as calcium, magnesium or aluminum, particularly where a non-ionic surfactant was not employed in combination with the anionic surfactant.

Latices produced by the process of this invention have a far lower surfactant content than latices produced by the teachings of the prior art in which a high content of surfactant is essential to provide adequate stability. Thus, latices of this invention will typically have a total surfactant content of less than 5 weight per cent, based on total weight of solids in the latex, whereas the latex products known to the art have typically exhib ted a total surfactant content of as high as 10 to 15 weight per cent, or more, on the same basis.

The ethylene interpolymers of this invention are copolymers, terpolymers, or higher interpolymers, containing as essential components both ethylene and a carboxylic acid as hereinbefore described. The carboxylic acid promotes latex stability and improves polymer properties. The optional incorporation of a copolymerizable monomer, as hereinbefore described, usually results in a decrease in the crystallinity of the polymer with a resultant lowering of polymer stiffness and consequent improvement in flexibility, tensile strength and elongation as well as reduction in the temperature required for fusion or film formation. If desired, the optional copolymerizable monomer may be a cross-linkable monomer, whereby improvement in such properties as water and solvent resistance may be achieved. The interpolymers produced by the process of this invention are not completely or even substantially uniform in composition in view of the differences in rate of reaction of the various monomers and in their ability to diffuse into the growing polymer particle. They may include a minor amount of gel-like material as a result of long chain branching or cross-linking. Both free carboxyl groups and salt groups resulting from ionic interaction between the carboxyl groups and metal ions, derived from the catalyst, or from the surfactant, or from the base which is added to increase the pH of the latex, may be expected to be present upon evaporation of the water from the latex after formation of a coating.

The unique feature of the ethylene interpolymer latices of this invention is that they not only exhibit excellent latex properties, as described above, but that at the same time the properties of the polymer meet or exceed the requirements necessary for utilization in coating applications. It is ordinarily not necessary to concentrate the latex, i.e. to increase the solids content by removal of part of the water, prior to use but rather the latex may be utilized directly in the form in which it is produced. It may, of course, be concentrated in this manner if desired. Except as otherwise indicated, all polymer properties set forth herein are composite properties of all the solids contained in the latex, i.e. they represent properties of the residue remaining after evaporation of all water with no attempt having been made to wash out the surfactant

prior to measurement of the property.

Ethylene interpolymers within the scope of this invention exhibit physical properties extending over a broad spectrum, with the properties of a particular polymer depending upon both its composition and the process conditions employed in its production. The copolymers of low carboxylic acid content, e.g. copolymers composed of ethylene and acrylic acid and containing up to 10 per cent by weight of acrylic acid, are tough and strong and will form a film substantially equivalent in performance to extruded film from bulk polymerized polyethylene. They exhibit far higher ultimate tensile strength and ultimate elongation than ethylene polymers available in latex form heretofore and are particularly distinguished from the prior art in this respect, since stable ethylene polymer latices heretofore produced directly by emulsion polymerization have invariably been composed of polymer which was weak and brittle. Typical ethylene/acrylic acid copolymers produced by the method of this invention have ultimate tensile strength of as high as 2000 psi., or higher, with ultimate elongation of as much as 200 per cent, or more. Terpolymers of ethylene, acrylic acid and, for example, vinyl acetate or ethyl acrylate, in substantial proportion, are of lower crystallinity than ethylene/acrylic acid copolymers and exhibit the characteristics of a soft polymer capable of undergoing film formation at relatively low temperatures.

The ethylene interpolymer latices of this invention find utility in a wide variety of applications. They may be used, for example, as barrier coatings for paper, paperboard and other substrates; as components of waxes and polishes; as warp sizes; as textile softeners; and so forth.

In one particular aspect, the present invention relates to paper or paperboard having a barrier coating formed from the ethylene interpolymer latices described herein. Such products exhibit good grease and oil resistance; good resistance to water, acids, and moisture vapor; good electrical conductivity; adhesiveness; ability to heat seal; and good printability and ink holdout. They find particular utility as decorative papers; as packaging materials for foods; as paper cups or plates; as shipping containers, and so forth. By appropriate selection of the interpolymer latex, coated paper products that are the equivalent of those obtained heretofore only through the use of melt-extrusion techniques can be produced.

The ethylene interpolymer latices described herein may be readily applied to paper and paperboard using coating equipment commonly found in a paper mill. Their low viscosity and good stability permits them to be pumped without difficulty and to be applied at the size press or calender stack. They may be applied with an air knife coater or, by addition of a small amount of a thickening agent such as hydroxyethyl cellulose to increase viscosity, with a trailing blade coater. After application of the latex to the paper or paperboard, neat is applied, e.g. temperatures in the range of 125° C. to 200° C., to effect evaporation of the water and fusion of the latex particles. One or more coats of any desired weight may be applied to the paper or paperboard.

The invention is further illustrated by the following specific examples of its practice. In the examples, the monomers, water, surfactant and catalyst were continuously pumped to a high pressure stainless steel reactor (in some instances the carboxylic acid was introduced in admixture with the other comonomer, in others as a solution in water or as a solution in an organic diluent such as toluene), whose contents were thoroughly agitated by three sets of flat bladed, high speed, radial turbines, and latex and unreacted monomers were continuously withdrawn from the reactor through a letdown valve which served as the pressure regulator for the reactor. In certain of the examples, molecular weight regulators, such as acetaldehyde or glycol ethers, were added in minor amounts. In each instance, at latex was collected in a cyclone separator from which gaseous ethylene was vented. The process was operated on a heat balance with the reaction being controlled so that the heat of polymerization would equal the available sensible heat capacity of the feed streams plus the heat which could be removed from the reactor through the cooling surfaces. Cooling was effected by circulation of a liquid cooling medium through an external jacket surrounding the high pressure reactor.

The process conditions utilized are summarized for convenience in Table I below, while latex properties are summarized in Table II, and polymer properties in Table III. In every instance, the latex exhibited good stability characteristics as hereinbefore described.

TABLE I

Example No.	Temperature (°C.)	Pressure (psig)	Monomers Compound	Monomers Feed Rate (lbs/hr/ft³)	Diluent Compound	Diluent Feed Rate (lbs/hr/ft³)	Water (lbs/hr/ft³)	Catalyst Compound	Catalyst Feed Rate (lbs/hr/ft³)	Surfactant Compound	Surfactant Feed Rate (lbs/hr/ft³)	Ethylene Conversion (%)	Space Productivity (lbs/hr/ft³)
1	140	21,000	Ethylene / Acrylic Acid	170 / 6.5	Toluene	4.3	123	$K_2S_2O_8$	0.40	SDBS	4.1	59	106
2	140	16,000 –17,600	Ethylene / Acrylic Acid	115 / 3.4	Toluene	2.3	83.4	$K_2S_2O_8$	0.37	SDBS	2.3	75.7	90
3	140	20,000	Ethylene / Acrylic Acid	176 / 7.6	Toluene	5.1	125	$K_2S_2O_8$	0.40	STS	3.4	51	98
4	140	22,000 –23,000	Ethylene / Acrylic Acid	156 / 4.0	Toluene	2.7	84	$K_2S_2O_8$	0.28	SDBS + STS	1.3 / 0.9	68	110
5	150	12,400	Ethylene / Acrylic Acid	87 / 3.1	Water	14.4	61	$K_2S_2O_8$	0.38	IDBS + STS	1.6 / 1.1	53	49
6	140	19,000 –24,000	Ethylene / Acrylic Acid	154 / 6.8	Toluene	4.6	124	$K_2S_2O_8$	0.43	SDBS + STS	2.0 / 1.3	62	103
7	141	21,600	Ethylene / Acrylic Acid	176 / 9.1	Toluene	6.0	123	$K_2S_2O_8$	0.40	SDBS + STS	2.0 / 1.4	65	124

TABLE I (Continued)

Example No.	Temperature (°C.)	Pressure (psig)	Monomers Compound	Monomers Feed Rate lbs/hr/ft³	Diluent Compound	Diluent Feed Rate lbs/hr/ft³	Water lbs/hr/ft³	Catalyst Compound	Catalyst Feed Rate lbs/hr/ft³	Surfactant Compound	Surfactant Feed Rate lbs/hr/ft³	Ethylene Conversion (%)	Space Productivity (lbs/hr/ft³)
8(a)	142—144	19,000—26,000	Ethylene Acrylic Acid	204 9.4	Toluene	6.3	122	$K_2S_2O_8$	0.61	SDBS + STS	2.7 1.8	62.8	136
9	110	19,000—25,000	Ethylene Acrylic Acid Ethyl Acrylate	99 7.4 24	None	—	110	$K_2S_2O_8$	0.48	SDBS + STS	1.7 1.2	71.8	99
10	111	21,000—25,000	Ethylene Acrylic Acid Ethyl Acrylate	80 4.2 26	None	—	77	$K_2S_2O_8$	0.21	SDBS + STS	1.2 0.8	61.6	75
11	100	19,200	Ethylene Acrylic Acid Ethyl Acrylate	47 4.2 26	None	—	77	$K_2S_2O_8$	0.21	SDBS + STS	1.2 0.8	41.3	61
12	140	14,000 18,500	Ethylene Acrylic Acid	114 2.5	Toluene	1.7	86	$K_2S_2O_8$	0.38	SDBS + STS	1.4 0.9	74.4	87
13	140	18,000	Ethylene Acrylic Acid Ethyl Acrylate(b)	94 4.8 —	Toluene	3.2	77	$(NH_4)_2S_2O_8$	0.34	SDBS + STS	1.2 0.8	61.2	71

TABLE I (Continued)

Example No.	Temperature (°C.)	Pressure (psig)	Monomers Compound	Feed Rate (lbs/hr/ft³)	Diluent Compound	Feed Rate (lbs/hr/ft³)	Water (lbs/hr/ft³)	Catalyst Compound	Feed Rate (lbs/hr/ft³)	Surfactant Compound	Feed Rate (lbs/hr/ft³)	Ethylene Conversion (%)	Space Productivity (lbs/hr/ft³)
14(c)	110	22,000—23,000	Ethylene Methacrylic Acid Ethyl Acrylate	108 15.0 8.3	None	—	75.2	$K_2S_2O_8$	0.48	SOS + SDBS	1.3 1.8	46.5	71
15	140	13,000—25,000	Ethylene Methacrylic Acid	106 2.8	Water	16	55	$K_2S_2O_8$	0.31	STS + SDBS	0.7 1.1	57.5	63
16	140	17,000—21,500	Ethylene Itaconic Acid	111 2.6	Water	30	52	$K_2S_2O_8$	0.35	STS + SDBS	0.9 1.2	46	52
17	140	27,500—28,200	Ethylene Acrylic Acid	78 8.8	Toluene	5.8	64	$K_2S_2O_8$	0.52	STS + SDBS	0.7 1.0	54	50
18	142	18,500—22,000	Ethylene Acrylic Acid	87 12.6	Toluene	9.2	78	$K_2S_2O_8$	0.54	STS + SDBS	1.5 2.2	60	62
19	140	19,000	Ethylene Acrylic Acid	128 2.9	Toluene	1.9	122	$K_2S_2O_8$	0.25	SOS + SDBS	0.4 0.7	76	51

TABLE I (Continued)

Example No.	Temperature (°C.)	Pressure (psig)	Monomers Compound	Feed Rate (lbs/hr/ft³)	Diluent Compound	Feed Rate (lbs/hr/ft³)	Water (lbs/hr/ft³)	Catalyst Compound	Feed Rate (lbs/hr/ft³)	Surfactant Compound	Feed Rate (lbs/hr/ft³)	Ethylene Conversion (%)	Space Productivity (lbs/hr/ft³)
20	110	19,500—22,000	Ethylene Acrylic Acid Ethyl Acrylate	39 3.7 36.0	None	—	75	$K_2S_2O_8$	0.68	SOS + N	2.2 0.7	76	71
21	138	17,800—19,000	Ethylene Acrylic Acid Bicyclo-[2.2.1]hept-2-ene	~97 2.9 9.5	Benzene + Toluene	4.1 1.9	80	$K_2S_2O_8$	0.27	STS + SDBS	0.9 1.3	40(d)	51
22	137	24,000—27,500	Ethylene Acrylic Acid Vinyl Chloride	100 4.9 3.5	Toluene	3.2	75	$K_2S_2O_8$	0.25	SDBS + STS	1.2 0.8	63	70
23	139	20,500	Ethylene Acrylic Acid Vinylidene Chloride	105 1.5 32.8	Toluene	1.0	76	$K_2S_2O_8$	0.67	SDBS + STS	1.2 0.8	48	70
24(e)	100	19,000	Ethylene Acrylic Acid Vinyl Acetate	71 2.8 22.6	None	—	77	$K_2S_2O_8$	0.21	SDBS + STS	1.2 0.85	64	58

TABLE I (Continued)

Example No.	Temperature (°C.)	Pressure (psig)	Monomers Compound	Feed Rate (lbs/hr/ft³)	Diluent Compound	Feed Rate (lbs/hr/ft³)	Water (lbs/hr/ft³)	Catalyst Compound	Feed Rate (lbs/hr/ft³)	Surfactant Compound	Feed Rate (lbs/hr/ft³)	Ethylene Conversion (%)	Space Productivity (lbs/hr/ft³)
25	110	22,000	Ethylene	~37	None	—	82	$K_2S_2O_8$	0.37	SOS + SDBS	2.1 / 1.1	65(d)	59
			Acrylic Acid	3.0									
			Ethyl Acrylate	32.8									
			Glycidyl Acrylate	1.8									
26	100	26,000	Ethylene	63	None	—	80	$K_2S_2O_8$	0.35	SLS + N	1.5 / 1.1	52	60
			Acrylic Acid	3.0									
			2-Ethylhexyl Acrylate	32.5									

(a) Acetaldehyde, at a rate of 1.4 lbs/hr/ft³, and the ethyl monoether of ethylene glycol, at a rate of 13.6 lbs/hr/ft³, added as molecular weight regulators
(b) Exact amount of ethyl acrylate not determined
(c) Acetaldehyde, at a rate of 2.2 lbs/hr/ft³, added as molecular weight regulator
(d) Estimated minimum value
(e) Sodium acetate, at a rate of 0.008 lbs/hr/ft³, added to maintain pH at 2.8

SDBS — Sodium dodecylbenzenesulfonate
STS — Sodium bis(tridecyl)sulfosuccinate
SOS — Sodium bis(octyl)sulfosuccinate
SLS — Sodium lauryl sulfate
N — Nonyl phenyl polyethylene glycol ether (15 moles ethylene oxide)
IDBS — Isopropylamine salt of dodecylbenzenesulfonic acid

TABLE II

Example No.	Total Solids (%)	Viscosity (cps at 100 rpm)	Seed Content (ppm on 250 mesh)(a)	Average Particle Size (microns)	Surfactant Content (wt. %)(b)
1	51.0	66	70	0.1—0.5	3.7
2	54.7	33	600	0.4	2.45
3	48.7	100	170	0.1—0.5	3.3
4	61.0	148	730	—	1.97
5	42.4	—	—	—	5.2
6	49.0	60	10 (c)	0.4	3.0
7	52.9	103	60	0.49	2.7
8	53.7	134	180	0.54	3.0
9	50.6	98	1440	0.34	2.85
10	50.6	172	40	0.44	2.7
11	44.7	130	120	—	3.7
12	54.2	94	640	0.46	2.6
13	50.0	211	400	—	3.0
14	52.6	256	380	—	4.2
15	49.0	58	200	—	2.8
16	45.4	88	3180	—	3.9

TABLE II (Continued)

Example No.	Total Solids (%)	Viscosity (cps at 100 rpm)	Seed Content (ppm on 250 mesh) (a)	Average Particle Size (microns)	Surfactant Content (wt %) (b)
17	45.9	178	160	—	3.3
18	46.5	140	140	—	5.5
19	29.7	—	16	0.40	2.1
20	45	64	300	0.20	3.9
21	42.3	69	60 (c)	—	4.2
22	49.8	54	130 (c)	—	2.8
23	49.6	608	600	—	2.8
24	45.1	47	220	0.41	3.4
25	47.3	66	180	—	5.1
26	39.3	267	380	—	4.1

(a) Based on the total weight of the latex

(b) Based on total solids in latex

(c) On 200 mesh screen

TABLE III

Example No.	Composition of Polymer		Melt Index at 202 psi (dg/min)	Stiffness (psi)	Ultimate Elongation (%)	Ultimate Tensile Strength (psi)	Hardness Shore A	Density (gm/cc)	Filming Temperature (°C.)
	Monomer	Wt. %							
1	Ethylene Acrylic Acid	93.8 6.2	13	24,700	90	1610	—	0.940	—
2	Ethylene Acrylic Acid	96.1 3.9	1.4	—	65	1300	—	0.934	—
3	Ethylene Acrylic Acid	92.3 7.7	9	25,800	140	1775	—	0.945	—
4	Ethylene Acrylic Acid	96.3 3.7	—	—	—	—	—	—	—
5	Ethylene Acrylic Acid	93.7 6.3	—	—	78	1575	—	0.931	—
6	Ethylene Acrylic Acid	93.3 6.7	2.7	24,700	180	1860	96	0.944	90—105
7	Ethylene Acrylic Acid	92.6 7.4	1.5	21,500	67	1533	—	0.942	—
8	Ethylene Acrylic Acid	93.1 6.9	259 (a)	27,500	78	1480	94	0.955	90—105
9	Ethylene Acrylic Acid Ethyl Acrylate	70.5 7.5 22.0	0.16	900	135	460	—	—	80—95

TABLE III (Continued)

Example No.	Composition of Polymer Monomer	Wt. %	Melt Index at 202 psi (dg/min)	Stiffness (psi)	Ultimate Elongation (%)	Ultimate Tensile Strength (psi)	Hardness Shore A	Density (gm/cc)	Filming Temperature (°C.)
10	Ethylene Acrylic Acid Ethyl Acrylate	66.3 5.7 28.0	0.3	800	205	425	59	0.953	50—70
11	Ethylene Acrylic Acid Ethyl Acrylate	31.2 4.3 64.5	0.4	<100	290	58	—	1.02	—
12	Ethylene Acrylic Acid	97.1 2.9	6.0	18,500	46	1400	—	0.934	—
13	Ethylene Acrylic Acid Ethyl Acrylate	~81.2 ~6.8 ~12.0	25	12,200	35	1100	—	0.940	—
14	Ethylene Methacrylic Acid Ethyl Acrylate	70.9 16.7 12.4	230 (a)	2850	440	2100	—	0.974	—
15	Ethylene Methacrylic Acid	— —	5.6	17,800	95	1370	—	0.932	—
16	Ethylene Itaconic Acid	98.6 1.4	0.1	29,950	75	1980	—	0.945	—
17	Ethylene Acrylic Acid	84.9 15.1	3.2	18,600	148	1890	—	0.969	—

TABLE III (Continued)

Example No.	Composition of Polymer		Melt Index at 202 psi (dg/min)	Stiffness (psi)	Ultimate Elongation (%)	Ultimate Tensile Strength (psi)	Hardness Shore A	Density (gm/cc)	Filming Temperature (°C.)
	Monomer	Wt. %							
18	Ethylene Acrylic Acid	83.2 16.8	5.5	16,200	220	2115	—	0.967	—
19	Ethylene Acrylic Acid	95.0 5.0	—	—	—	—	—	—	—
20	Ethylene Acrylic Acid Ethyl Acrylate	41.7 5.2 53.1	0.70	40	250	38	—	1.018	<25
21	Ethylene Acrylic Acid Bicyclo[2.2.1]-hept-2-ene	75.9 (b) 5.6 (c) 18.5 (c)	0.57	10,000	75	1190	—	0.947	—
22	Ethylene Acrylic Acid Vinyl Chloride	90.9 5.5 3.6	0.8	19,000	155	1430	—	0.946	—
23	Ethylene Acrylic Acid Vinylidene Chloride	71.3 2.0 26.7	90	3300	190	413	—	1.038	—
24	Ethylene Acrylic Acid Vinyl Acetate	78.5 4.9 16.6	0.92	4200	370	1355	84	0.963	60—90

TABLE III (Continued)

Example No.	Composition of Polymer Monomer	Wt. %	Melt Index at 202 psi (dg/min)	Stiffness (psi)	Ultimate Elongation (%)	Ultimate Tensile Strength (psi)	Hardness Shore A	Density (gm/cc)	Filming Temperature (°C.)
25	Ethylene Acrylic Acid Ethyl Acrylate Glycidyl Acrylate	36.3 (b) 5.0 (c) 55.6 (c) 3.1 (c)	0 (d)	45	200	66	—	—	—
26	Ethylene Acrylic Acid 2-Ethylhexyl Acrylate	54.4 (b) 5.6 (c) 40.0 (c)	0.32	400	100	195	—	—	—

(a) Measured at 44 psi

(b) Estimated minimum value

(c) Estimated maximum value

(d) Cross-linked polymer and therefore no melt flow

EXAMPLE 27

The latex described in Example 7 hereinabove was applied to a machine glazed kraft paper and to a bleached sulfite food board by use of a wire wound rod and fused by heating for 5 minutes a 125° C. The following properties were measured:

Coating Weight—determined by weighing the sheet before and after coating and calculated on a ream basis.

Pinhole Rating—an area about 2″ × 11″ is brushed with methanol dyed with methylene blue. A rating of "0" indicates 0 to 1 pinholes, a rating of "1" indicates 2 to 3 pinholes, a rating of "2" indicates 4 to 6 pinholes,

and a rating of "3" indicates more than 6 pinholes.

Gloss—75° specular gloss measured with a Gardner glossmeter.

Blocking—sheets are placed face to face for 16 hours at 40° C. in a 100% humidity cabinet under a pressure of 1 psi. A rating of "0" indicates no blocking, a rating of "1" indicates very slight blocking, a rating of "2" indicates marks in film, and a rating of "3" indicates fiber tear.

Heat Seal—sheets are pressed together face to face for one second at 20 psi. and 100° C. Strong bond indicates tearing of a sheet when separation is attempted.

Turpentine Resistance—determined as described in TAPPI test T 454 M 60 except that test is continued for 24 hours and samples are observed after 1, 16 and 24 hours. If no penetration occurs, the rating is 24+, otherwise the rating is the number of hours required to penetrate.

Peanut Oil Resistance—carried out in the same manner as the turpentine resistance test.

Lactic Acid Resistance—20% lactic acid at 120° F. is maintained in contact with the coating for 5 minutes. If no penetration occurs, the rating is 5+, otherwise the rating is the number of minutes required to penetrate.

Score Failure—the coated paperboard is scored in accordance with TAPPI test RC 66 and folded 180° towards the coated side. The crease is painted with dyed methanol and rated in the same manner as described above with reference to pinhole rating.

Glueability—determined in accordance with TAPPI Monograph No. 26; the value reported being the number of minutes required for a standard boxboard adhesive to develop a bond strong enough to give fiber tear when an attempt is made to separate it.

Contact Angle—determined with a goniometer.

Moisture Vapor Transmission—(MVT)—determined in accordance with ASTM method D814—44T.

Results obtained are summarized below:

Coated paper (one coat)

Coating weight (lbs/3300 ft²)	—	7.3
Pinhole rating	—	3
75° gloss (%)	—	48
Blocking	—	0
Heat seal	—	strong bond

Coated paper (two coats)

Coating weight (lbs/3300 ft²)	—	14
Pinhole rating	—	0
75° gloss (%)	—	67
Turpentine resistance (hrs.)	—	24+
Peanut oil resistance (hrs.)	—	24+
Lactic acid resistance (min.)	—	5+
MVT — flat	—	1.8
MVT — creased	—	2.7

Coated paperboard

Coating weight (lbs/1000 ft²)	—	2.6
Pinhole rating	—	3
75° gloss (%)	—	45
Contact angle	—	27
Glueability (mins.)	—	6
Score failure (two coats)	—	1

WHAT WE CLAIM IS:—

1. A continuous process for production of an ethylene interpolymer latex which comprises

(1) continuously charging to a reactor, in which substantially uniform conditions of temperature, pressure and concentration are maintained throughout with a temperature in the range of 100° C. to 160° C. and a pressure of at least 5,000 psig., the following materials:

a) polymerizable monomer at a rate of at least 50 lbs. per hour per cubic foot of reactor volume, said polymerizable monomer comprising at least 50 mole per cent ethylene and from 0.2 to 15 mole per cent of at least one α-β-ethylenically unsaturated carboxylic acid of 3 to 8 carbon atoms and, as any remaining balance, at least one other copolymerizable monoethylenically unsaturated monomer of 2 to 12 carbon atoms;

b) water at a rate of 0.3 to 3 lbs. per lb. of said polymerizable monomer undergoing conversion to polymer;

c) a persulfate catalyst which is ammonium persulfate or an alkali metal persulfate at a rate sufficient to provide a catalytically effective amount; and

d) a surfactant which is chemically stable and capable of forming abundant micelles under the conditions at which the process is

operated at a rate of 0.005 to 0.05 lbs. per lb. of said polymerizable monomer undergoing conversion to polymer;

the process conditions being so selected to provide a space productivity of at least 25 lbs. of polymer per hour per cubic foot of reactor volume, and

(2) continuously recovering the latex produced thereby.

2. A process as claimed in claim 1 in which the temperature is in the range of 110° C. to 150° C.

3. A process as claimed in claim 1 or 2 in which the pressure is in the range of 10,000 psig. to 30,000 psig.

4. A process as claimed in any of claims 1 to 3 in which the α-β-ethylenically unsaturated carboxylic acid is acrylic acid.

5. A process as claimed in any of claims 1 to 4 in which the copolymerizable monoethylenically unsaturated monomer is an acrylate.

6. A process as claimed in any of claims 1 to 4 in which the copolymerizable monoethylenically unsaturated monomer is a vinyl ester of an alkanoic monobasic acid having up to 4 carbon atoms.

7. A process as claimed in claim 4 in which the interpolymer is a copolymer of ethylene and acrylic acid.

8. A process as claimed in claim 7 in which the interpolymer is a copolymer consisting of at least 90 weight per cent ethylene and the balance acrylic acid.

9. A process as claimed in claim 5 in which the interpolymer is a terpolymer of ethylene, acrylic acid and ethyl acrylate.

10. A process as claimed in claim 6 in which the interpolymer is a terpolymer of ethylene, acrylic acid and vinyl acetate.

11. A process as claimed in any of claims 1 to 10 in which the polymerizable monomer is fed to the reactor at a rate of 100 to 300 lbs. per hour per cubic foot of reactor volume.

12. A process as claimed in any of claims 1 to 11 in which water is fed to the reactor at a rate of 0.8 to 1.5 lbs. per lb. of polymerizable monomer undergoing conversion to polymer.

13. A process as claimed in any of claims 1 to 12 in which the persulfate catalyst is potassium persulfate.

14. A process as claimed in any of claims 1 to 13 in which the persulfate catalyst is fed to the reactor at a rate of 0.02 lbs per lb. of polymerizable monomer undergoing conversion to polymer.

15. A process as claimed in claim 14 in which the persulfate catalyst is fed to the reactor at a rate of 0.002 to 0.007 lbs. per lb. of polymerizable monomer undergoing conversion to polymer.

16. A process as claimed in any of claims 1 to 15 in which the surfactant is a bis(alkyl)-sulfosuccinate.

17. A process as claimed in claim 16 in which the surfactant is sodium bis(tridecyl)-sulfosuccinate.

18. A process as claimed in any of claims 1 to 15 in which the surfactant is sodium dodecylbenzenesulfonate.

19. A process as claimed in any of claims 1 to 18 in which the surfactant is fed to the reactor at a rate of 0.01 to 0.03 lbs. per lb. of polymerizable monomer undergoing conversion to polymer.

20. A process as claimed in any of claims 1 to 19 in which the space productivity is at least 50 lbs. of polymer per hour per cubic foot of reactor volume.

21. A process as claimed in any of claims 1 to 20 in which the pH in the reactor is maintained at a level of below 4.

22. A continuous process for production of an ethylene/acrylic acid copolymer latex which comprises (1) continuously charging to a reactor, in which substantially uniform conditions of temperature, pressure and concentration are maintained throughout with a temperature in the range of 100° C. to 160° C. and a pressure of at least 5,000 psig., the following.

a) polymerizable monomer at a rate of at least 50 lbs. per hour per cubic foot of reactor volume, said polymerizable monomer consisting of 85 to 99.8 mole per cent ethylene and 15 to 0.2 mole per cent acrylic acid;

b) water at a rate of 0.3 to 3 lbs. per lb. of said polymerizable monomer undergoing conversion to polymer;

c) a persulfate catalyst which is ammonium persulfate or an alkali metal persulfate at a rate of 0.001 to 0.02 lbs. per lb. of polymerizable monomer undergoing conversion to polymer; and

d) a surfactant which is an amine salt of an alkylaryl sulfonate, an alkali metal salt of an alkylaryl sulfonate or a bis(alkyl)sulfosuccinate, at a rate of 0.005 to 0.05 lbs. per lb. of said polymerizable monomer undergoing conversion to polymer;

the process conditions being so selected to provide a space productivity of at least 25 lbs. of polymer per hour per cubic foot of reactor volume, and (2) continuously recovering the latex produced thereby.

23. A continuous process for the production of an ethylene interpolymer latex substantially as hereinbefore described with particular reference to any of the foregoing Examples.

24. An ethylene interpolymer latex whenever produced by a process as herein described and claimed.

25. An article of manufacture comprising a paper substrate having a coating thereon, said coating having been produced by applying an

ethylene interpolymer latex as claimed in claim
24 to said paper substrate.

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